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Lead(II)-Induced Allosteric G-Quadruplex DNAzyme as a Colorimetric and Chemiluminescence Sensor for Highly Sensitive and Selective Pb^{2+} Detection

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The lead ion (Pb^{2+}) has been proven to induce a conformational change of K^+-stabilized G-quadruplex DNAzyme and inhibit the peroxidase-like activity [Li, T.; Wang, E.; Dong, S. *J. Am. Chem. Soc.* 2009, *131*, 15082−15083]. This provides a rationale for utilizing Pb^{2+}-induced allosteric G-quadruplex DNAzyme to probe aqueous Pb^{2+}. Here, we choose a common G-quadruplex DNAzyme named PS2.M to develop a novel Pb^{2+} sensor with two detection means: colorimetry and chemiluminescence (CL). In the presence of K^+, PS2.M (with hemin as a cofactor) exhibits a superior DNAzyme activity and effectively catalyzes the H_2O_2-mediated oxidation of 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) or luminol, which results in a color change or generates CL emission. Upon the addition of Pb^{2+}, K^+-stabilized PS2.M is induced to convert to the Pb^{2+}-stabilized structure with higher stability but lower DNAzyme activity, which is reflected by an obvious increase in DNA melting temperature but a sharp decrease in readout signal. This allows us to utilize PS2.M for quantitative analysis of aqueous Pb^{2+} using the ABTS−H_2O_2 colorimetric system and luminol−H_2O_2 CL system. In each case, the readout signal is linearly dependent on the logarithm of Pb^{2+} concentration within a certain range. Nevertheless, two sensing systems provide different sensitivity for Pb^{2+} analysis. With colorimetry, Pb^{2+} can be detected at a level of 32 nM (∼7 ppb), whereas the detection limit of Pb^{2+} is 1 nM (0.2 ppb) when utilizing the CL method. In addition to high sensitivity, the above sensing systems exhibit good selectivity for Pb^{2+} over other metal ions. These results demonstrate the facility and effectivity of our introduced DNAzyme-based sensor for quantitative Pb^{2+} analysis.

Heavy-metal pollution in the environment attracts increasing attention, because it has severely adverse effect on human health. It is a challenge to facilely monitor these toxic metals below the defined toxic level. Toward this goal, many methods for metal ion analysis have been developed.[1−3] Of particular interest has been the detection of Pb^{2+}, which is an important environmental pollutant. Over the past 10 years, many highly sensitive and selective Pb^{2+} sensors have been developed, most of which are primarily based on a Pb^{2+}-specific RNA-cleaving DNAzyme (i.e., 8-17).[4−13] In fact, the 8-17 DNAzyme or its analogue now becomes an indispensable sensing element for the construction of nucleic acid-based Pb^{2+} sensors. As a substitute, here, we introduce a Pb^{2+}-induced allosteric G-quadruplex DNAzyme, which can serve as a Pb^{2+} sensor that operates quite facilely.

G-quadruplexes are four-stranded DNA structures stabilized by coordination cations, e.g., K^+ and Na^+. Interestingly, a few of K^+-stabilized G-quadruplexes (with hemin as a co-factor) exhibit superior peroxidase-like activity and effectively catalyze the H_2O_2-mediated oxidation of 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS)[14,15] or luminol.[16−19] This enables the utilization of these G-quadruplex DNAzymes to develop colorimetric or chemiluminescence (CL) metal ion

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sensors.[12,20−24] In comparison with K^+, Pb^{2+} has a higher efficiency with regard to stabilizing G-quadruplexes,[25,26] because the Pb^{2+}-stabilized quadruplex structures are more compact than the K^+-stabilized ones.[27,28] These structural features allow Pb^{2+} to induce K^+-stabilized G-quadruplex DNAzymes to undergo a conformational change, accompanied by a decrease in the catalytic activity.[29] For this reason, here, we utilize a widely used G-quadruplex DNAzyme (i.e., PS2.M) to develop a novel sensor for Pb^{2+} analysis.

In this work, circular dichroism (CD) measurement and UV−vis absorption spectroscopy are utilized to indicate Pb^{2+}-induced changes in G-quadruplex conformation and DNAzyme activity. Colorimetric and CL detection of aqueous Pb^{2+} is performed in the ABTS−H_2O_2 and luminol−H_2O_2 reaction systems, respectively. High sensitivity and selectivity for quantitative Pb^{2+} analysis are achieved.

EXPERIMENTAL SECTION

Oligonucleotide and Chemicals. The purified G-rich oligonucleotide (PS2.M: GTGGGTAGGGCGGGTTGG) and hemin (from bovine) were obtained from Sangon Biotechnology Co., Ltd. (Shanghai, PRC). ABTS and luminol were purchased from Sigma−Aldrich (St. Louis, MO). All reagents were used as received without further purification. The stock solution of oligonucleotide (200 μM) was prepared in 10 mM Tris-Ac buffer (pH 8.0) and accurately quantified using UV−vis absorption spectroscopy with the following extinction coefficients ($\varepsilon_{260\ nm}$, expressed in units of $M^{-1}\ cm^{-1}$) for each nucleotide: A = 15 400, G = 11 500, C = 7400, T = 8700. The stock solution of hemin (5 mM) was prepared in dimethyl sulfoxide (DMSO), stored in darkness at −20 °C. Before use, the oligonucleotide and hemin solutions were diluted to required concentrations with the working buffer.

Instrumentation. A Cary 500 Scan UV−vis-NIR spectrophotometer (Varian, USA) was used to collect the absorption spectra of the radical anion $ABTS^{\bullet-}$ (i.e., the product of ABTS oxidation by H_2O_2). A Model MCDR-A Chemiluminescence Analyzer System (Xi'An Remax Analytical Instrument Co. Ltd., Xi'An, PRC) was used to collect the CL emission of luminol oxidation by H_2O_2. A JASCO Model J-810 spectropolarimeter (Tokyo, Japan) was utilized to collect the CD spectra of G-quadruplexes stabilized by different coordination cations.

Preparation of K^+- or Pb^{2+}-stabilized G-quadruplexes. The DNA solutions were heated at 88 °C for 10 min to dissociate any intermolecular interaction, and gradually cooled to room temperature. Then, appropriate concentration of KAc or $Pb(NO_3)_2$ was added into the DNA solution, allowing DNA sequences to properly fold for 40 min to form the quadruplex structures stabilized by K^+ or Pb^{2+}. Finally, the G-quadruplexes were incubated with hemin for over 1 h in 10 mM Tric-Ac buffer (pH 8.1) containing 10 mM KAc and 0.05% (w/v) Triton X-100. It would allow the formation of hemin−G-quadruplex complexes.

CD Measurements. The CD spectra of PS2.M (10 μM) were collected with the JASCO spectropolarimeter in the Tris-Ac buffer (pH 8.1) containing 10 mM KAc and different concentrations (0−40 μM) of $Pb(NO_3)_2$. The optical chamber (1 cm path length, 1 mL volume) was deoxygenated with dry purified nitrogen (99.99%) before use and kept the nitrogen atmosphere during experiments. Three scans (100 nm/min) from 240 to 360 at 0.1 nm intervals were accumulated and averaged. The background of the buffer solution was subtracted from the CD data.

UV−vis Spectroscopic Analysis. Colorimetric detection of Pb^{2+} utilizing G-quadruplex DNAzyme was performed in the ABTS−H_2O_2 reaction system at room temperature. In a typical experiment, the peroxidation reaction was initiated by the addition of 10 μL of 60 mM H_2O_2 to 990 μL of Tris-Ac solution (pH 8.1) containing 1.8 mM ABTS, 0.2 μM hemin, 0.2 μM G-quadruplex DNA, 0.05% (w/v) Triton X-100, 10 mM KAc, and different concentrations of $Pb(NO_3)_2$. The absorption spectra of the reaction mixture were recorded within 4 min with a UV−vis−NIR spectrophotometer in the wavelength range from 500 nm to 390 nm.

Chemiluminescence Analysis. CL detection of Pb^{2+} utilizing G-quadruplex DNAzyme was performed in the luminol−H_2O_2 reaction system at room temperature. Briefly, to 980 μL Tris-Ac solution (pH 8.1) containing 0.5 mM luminol, 10 mM KAc and 0.05% Triton X-100 was added 10 μL of 200 mM H_2O_2, followed by 10 μL of the 0.1 μM hemin and 1 μM PS2.M mixture that contains 10 mM KAc and different concentrations of $Pb(NO_3)_2$. The CL emission within 200 s was collected by the MCDR-A System. The voltage of PMT was set at 500 V.

DNA Melting Experiments. The UV melting curves of G-quadruplex DNAs (2.5 μM) in 10 mM Tris-Ac buffer (pH 8.1) containing 10 mM KAc were recorded by a UV−vis−NIR spectrophotometer equipped with a temperature-controlled water bath. The absorbance was always monitored at 295 nm, which is the characteristic absorption of the quadruplex structures.[30] In a typical experiment, 1 mL of sample solution was added into a 1-cm path length quartz cuvette, and then covered with a layer of paraffin oil to prevent evaporation. The solution was held at 30 °C for 2 min, and then slowly heated to 90 °C with a rate of 0.5 °C/min. Data were collected every 0.1 °C. The background of the buffer solution was subtracted from the collected data. The resulting melting curves were analyzed to obtain the melting temperature (T_m) via the first derivative.

Safety Considerations. Because Pb^{2+} and most of the tested heavy metals are highly toxic and have adverse effects on human health, all experiments involving in heavy-metal ions should be performed with protective gloves. The waste solutions that contain heavy-metal ions should be collectively reclaimed to avoid polluting the environment.

RESULTS AND DISCUSSION

Principle of Sensing Pb^{2+} via G-quadruplex DNAzyme. Because K^+ and Pb^{2+} have distinct effects on the peroxidase-like activity of G-quadruplex DNAzymes,[29] here, we utilize K^+-stabilized PS2.M to sense aqueous Pb^{2+} with two detection

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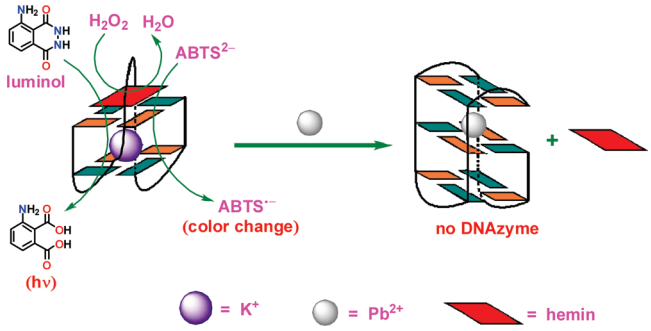

Figure 1. Schematic of utilizing Pb^{2+}-induced allosteric G-quadruplex DNAzyme, PS2.M, for label-free colorimetric and CL detection of Pb^{2+}.

means (see Figure 1). In the presence of K^+, PS2.M folds into a unimolecular G-quadruplex.[31,32] This K^+-stabilized quadruplex structure binds hemin with high affinity,[15] resulting in a complex that mimics the horseradish peroxidase and catalyzes the H_2O_2-mediated oxidation of ABTS or luminol to generate color change or CL emission. In contrast, the Pb^{2+}-stabilized PS2.M does not bind hemin, thereby exhibiting no DNAzyme activity.[29] Very importantly, here, we find that Pb^{2+} is able to induce K^+-stabilized PS2.M to undergo a conformation transition, which is accompanied by a sharp decrease in the DNAzyme activity monitored in the ABTS$-H_2O_2$ or luminol$-H_2O_2$ reaction system. This enables PS2.M to serve as the sensing element for label-free colorimetric or CL detection of Pb^{2+}.

Because the CD spectrum of Pb^{2+}-stabilized PS2.M differs from that of the K^+-stabilized PS2.M,[29] here, we utilize CD measurements to monitor the structural change of PS2.M (see Figure 2a). In the absence of Pb^{2+}, the K^+-stabilized PS2.M has a strong positive band near 295 nm in the CD spectrum. Upon the addition of Pb^{2+}, a positive peak appears at ~312 nm, which is the typical characteristic of Pb^{2+}-stabilized antiparallel G-quadruplexes.[25,26,29] As the concentration of Pb^{2+} increases, the peak near 312 nm becomes stronger, whereas that near 295 nm disappears gradually, indicating that PS2.M undergoes a conformation transition induced by Pb^{2+}. When the concentration of Pb^{2+} increases over 20 μM, only the Pb^{2+}-stabilized quadruplex structure exists in the solution. This demonstrates that Pb^{2+} binds PS2.M strongly enough to effectively compete against K^+, which is mainly attributed to great difference between the stability of two cation-stabilized G-quadruplexes. Generally, a Pb^{2+}-G-quadruplex complex has shorter M$-$O and O$-$O bonds, compared with those of the K^+-G-quadruplex.[27,28] For this reason, the Pb^{2+}-G-quadruplex usually has greater stability than the K^+-G-quadruplex.[26] Figure 2b shows that the T_m value of PS2.M increases by over 12 °C upon incubating with Pb^{2+}, which may rationally interpret why Pb^{2+} can competitively bind to PS2.M, even in the presence of ca. 1000-fold K^+.

However, for the G-quadruplex DNAzymes, high stability does not indicate high activity. The folded PS2.M has a superior peroxidase-like activity in the presence of K^+, whereas that of Pb^{2+}-

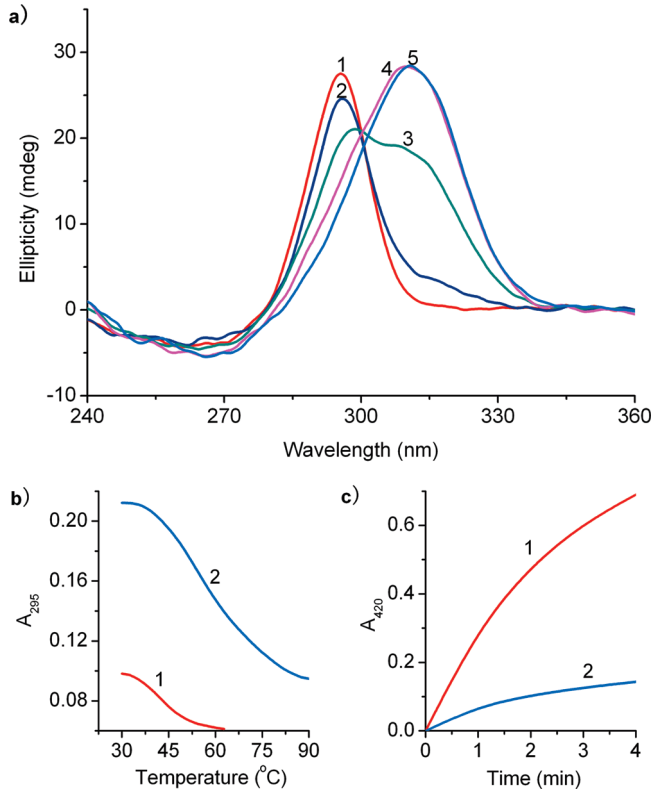

Figure 2. Structures and properties of PS2.M stabilized by K^+ and Pb^{2+}. (a) Conformational transition of PS2.M (stabilized by 10 mM K^+) upon adding different concentrations of Pb^{2+}: 0 μM (curve 1), 1 μM (curve 2), 5 μM (curve 3), 20 μM (curve 4), and 40 μM (curve 5). (b) UV melting curves of PS2.M stabilized by different cations: 10 mM K^+ (curve 1) and 10 mM K^+ and 40 μM Pb^{2+} (curve 2). (c) Kinetics curves for the ABTS$-H_2O_2$ reactions catalyzed by the hemin$-$PS2.M complex in the presence of different cations: 10 mM K^+ (curve 1) and 10 mM K^+ and 40 μM Pb^{2+} (curve 2). The absorbance was always monitored at 420 nm, which is the maximal absorption of the product $ABTS^{\bullet-}$.

stabilized PS2.M is poor (see Figure 2c). Although Pb^{2+} has an unusually high efficiency for stabilizing G-quadruplexes, this cation does not favor hemin binding and DNAzyme formation.[29] Likewise, another cation Sr^{2+} proved to have greater efficiency at stabilizing G-quadruplexes than K^+,[33] but it is also unfavorable for G-quadruplex DNAzymes (see Figure S1 in the Supporting Information). In contrast, K^+ at the millimolar level is found to be required for the superior catalytic behavior of PS2.M (see Figure S2 in the Supporting Information), consistent with previous observations.[14,15] This strongly suggests that only K^+-stabilized PS2.M provides suitable sites for hemin binding, which is very essential to the DNAzyme activity.[31]

The above observations clearly demonstrate Pb^{2+}-induced allosterism of PS2.M and well elucidate the ability of Pb^{2+} to deactivate the G-quadruplex DNAzyme. This provides a rationale for utilizing K^+-stabilized PS2.M to analyze Pb^{2+} quantitatively, using colorimetric and CL detection means.

Colorimetric Detection of Aqueous Pb^{2+}. In the DNAzyme-catalyzed ABTS$-H_2O_2$ reaction system, different concentrations of Pb^{2+} are analyzed via monitoring the change in absorption spectrum of the colored product $ABTS^{\bullet-}$, which has a maximal

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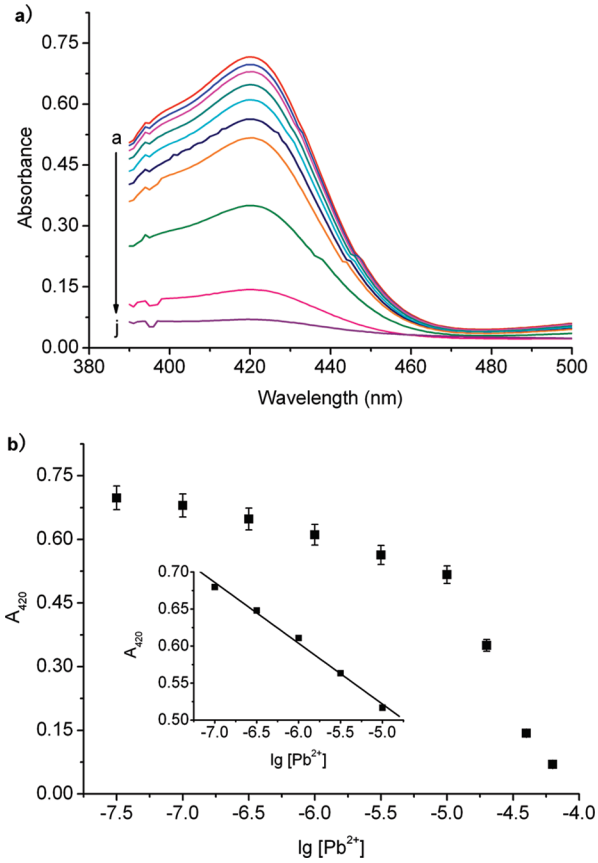

Figure 3. Utilization of K^+-stabilized PS2.M for colorimetric Pb^{2+} analysis in the ABTS−H_2O_2 system: (a) UV−vis absorption spectra (after 4 min) for utilizing 0.2 μM hemin-PS2.M to analyze different concentrations of Pb^{2+}: 0 nM (curve a), 32 nM (curve b), 100 nM (curve c), 320 nM (curve d), 1 μM (curve e), 3.2 μM (curve f), 10 μM (curve g), 20 μM (curve h), 40 μM (curve i), and 60 μM (curve j). (b) Dependence of the absorbance at 420 nm (A_{420}) on the logarithm of Pb^{2+} concentration. The inset shows a linear range from 10^{-7} M to 10^{-5} M.

absorption of ~420 nm (see Figure 3a). In the absence of Pb^{2+}, K^+-PS2.M has a superior catalytic activity toward the H_2O_2-mediated oxidation of ABTS, reflected by a strong absorbance (see curve a in Figure 3a). Upon the addition of an increasing amount of Pb^{2+}, there is a gradual decrease in readout signal. An obvious absorbance change is observed when 32 nM Pb^{2+} is added (see Figure 3a), namely, the detection limit for Pb^{2+} analysis with colorimetry is 32 nM (~7 ppb).

Figure 3b outlines the relationship between the Pb^{2+} concentration and absorbance at 420 nm (A_{420}), indicating a dependence of A_{420} on the logarithm of Pb^{2+} concentration. From this plot, it is observed that the absorbance decreases relatively slowly as Pb^{2+} concentration increases up to 10^{-5} M, whereas there is a sharp decrease when Pb^{2+} concentration is above 10^{-5} M. This suggests that there may be two steps in the Pb^{2+}-induced deactivation of G-quadruplex DNAzyme. Generally, K^+ is apt to be located in the cavity between two adjacent G-tetrads of a G-quadruplex and coordinate with eight carbonyl oxygen atoms of G residues from the G-tetrads.[34] Meanwhile, it can also bind to the G-quadruplex via interacting with carbonyl oxygen atoms of loop T residues.[35] These two coordination interactions are thought to occur in the K^+-stabilized structure of PS2.M, because it has a few loop T residues. Upon incubating Pb^{2+} with K^+-PS2.M, Pb^{2+} may be first located in the cavity between the G-tetrads, in place of K^+. During this process, the G residues and loop residues of PS2.M undergoes a rearrangement accompanied by a remarkable change in the polarity, which is reflected by CD spectra (see Figure 2a). This results in a decrease in the DNAzyme activity. However, in this case, K^+ can still bind to PS2.M via loop binding, which is favorable for the catalytic behavior of PS2.M. As the concentration of Pb^{2+} continues to increase, Pb^{2+} may replace K^+ to participate in the loop binding interaction. As a result, the DNAzyme is deactivated entirely. In contrast to the first step, this process does not involve structural rearrangement, thereby resulting in no obvious change in CD spectra. It provides a rational interpretation for why the DNAzyme activity is significantly decreased as the Pb^{2+} concentration increases from 20 μM to 40 μM (see Figure 3), whereas the CD spectrum of PS2.M is almost unchanged (see Figure 2a).

The inset of Figure 3b shows the calibration curve for quantitative analysis of aqueous Pb^{2+} with colorimetry. The absorbance is linearly dependent on the logarithm of Pb^{2+} concentration in the range from 10^{-7} M to 10^{-5} M ($R = 0.997$). The above observations demonstrate the G-quadruplex DNAzyme PS2.M can serve as a novel colorimetric sensor for sensitive Pb^{2+} detection.

CL Detection of Pb^{2+}. Likewise, quantitative Pb^{2+} analysis utilizing G-quadruplex DNAzyme is also performed in the luminol−H_2O_2 reaction system, because the DNAzyme activity also can be characterized by the CL method. Figure 4a shows the CL integral curves for analyzing different concentrations of Pb^{2+}. Just like that in the colorimetric system, the readout signal is gradually decreased upon incubating more and more Pb^{2+} with K^+-PS2.M. An obvious change of CL signal is achieved via the addition of 1 nM Pb^{2+}, indicating a detection limit of 1 nM (0.2 ppb) for CL detection of Pb^{2+}. This sensitivity is an order of magnitude higher than that of a previous counterpart,[12] and it is comparable to highly sensitive fluorescent Pb^{2+} sensors that have been reported recently.[36]

Figure 4b outlines the relationship between the Pb^{2+} concentration and integrated CL intensity (within 200 s), indicating a dependence of CL signal on the logarithm of Pb^{2+} concentration. Similar to the observation from Figure 3b, there are also two regions in this plot on the left and right of a point where the Pb^{2+} concentration is $10^{-6.5}$ M, which may be corresponding to two steps in the Pb^{2+}-induced deactivation of G-quadruplex DNAzyme. Note that, here, the concentrations of PS2.M and hemin are much lower than those in the colorimetric system described above, because of the higher sensitivity of CL method. This is a main reason why the CL system has a lower linear range (Figure 4b, inset), which is from 10^{-9} M to $10^{-6.5}$ M ($R = 0.99$), for quantitative Pb^{2+} analysis than the colorimetry.

Selectivity of G-quadruplex DNAzyme-based Pb^{2+} Sensor. To test the specificity of this Pb^{2+} sensor, other common metal ions are adopted in place of Pb^{2+} and added into the DNAzyme-

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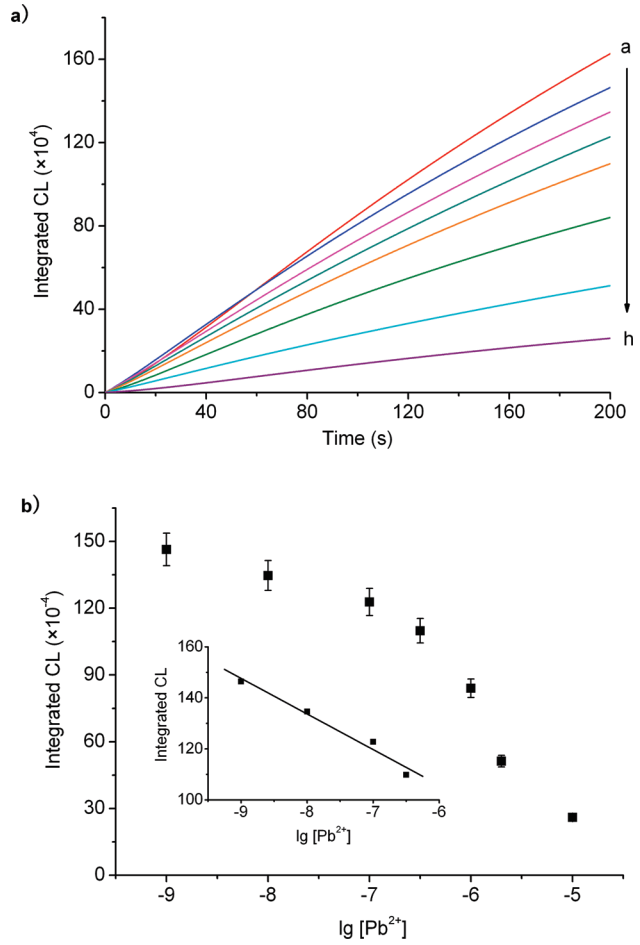

Figure 4. CL detection of Pb^{2+} using 10 nM PS2.M and 1 nM hemin in the luminol−H_2O_2 system: (a) CL integral curves for analyzing different concentrations of Pb^{2+}: 0 nM (curve a), 1 nM (curve b), 10 nM (curve c), 100 nM (curve d), 320 nM (curve e), 1 μM (curve f), 2 μM (curve g), and 10 μM (curve h). (b) Dependence of integrated CL intensity (within 200 s) on the logarithm of Pb^{2+} concentration. The inset shows a linear range from 10^{-9} M to $10^{-6.5}$ M.

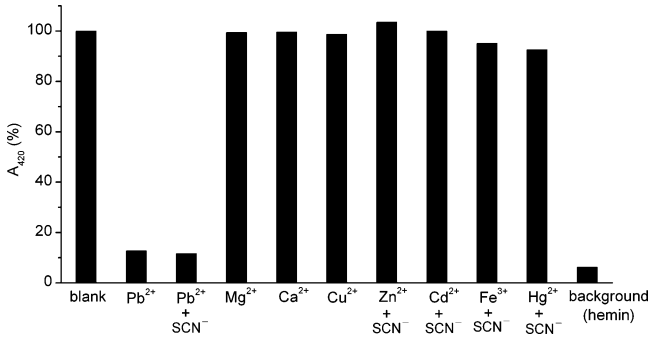

Figure 5. Selectivity of the DNAzyme-based Pb^{2+} sensor (0.2 μM PS2.M) over some common metal ions (60 μM), with the assistance of masking agent SCN^- (10 mM).

catalyzed ABTS−H_2O_2 system (see Figure 5). In our previous studies,[20,22] Hg^{2+} proved to inhibit the DNAzyme activity of T-containing G-quadruplexes due to the formation of T-Hg^{2+}-T base pairs. Because PS2.M contains a few T residues, it is conceivable that Hg^{2+} will interact with PS2.M and inhibit its DNAzyme activity, thereby having potential influence on the detection of Pb^{2+}. However, this interference can be overcome

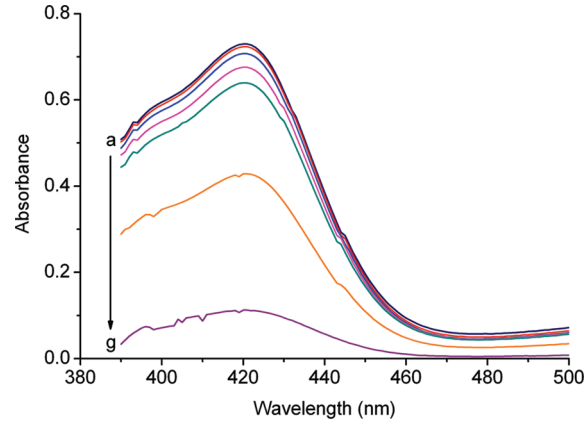

Figure 6. Application of the DNAzyme probe to the analysis of Pb^{2+} in freshwater sample: blank (curve a), lake water (curve b), lake water + 100 nM Pb^{2+} (curve c), lake water + 1 μM Pb^{2+} (curve d), lake water + 10 μM Pb^{2+} (curve e), lake water + 60 μM Pb^{2+} (curve f), and lake water + 100 μM Pb^{2+} (curve g).

by introduction of a chelator (e.g., CN^-) that is specific for Hg^{2+} against Pb^{2+}. This strategy has been successfully utilized to improve the specificity for Pb^{2+} detection.[36] However, CN^- is highly toxic, and its use for metal ion analysis will bring additional environmental contamination. Furthermore, CN^- is a strong ligand for Fe(III)-centered porphyrins,[37,38] and it will occupy the fifth and sixth coordination position of the Fe atom of hemin. This no longer allows terminal guanines of PS2.M to provide an axial coordination to hemin, as proposed previously.[31,39] As a result, the hemin−PS2.M complex no longer has the peroxidase-like activity. That is, CN^- is expected to have severe influence on the DNAzyme activity. In contrast, the activity of PS2.M is almost not affected by SCN^- (data not shown). For the above reasons, here we employ SCN^- rather than CN^- to mask Hg^{2+} and other potential interference ions. In this case, KSCN replaces KAc to provide the coordination cation K^+ and, meanwhile, introduce the chelator (10 mM SCN^-). Figure 5 shows the utilization of PS2.M for analyzing different metal ions in the presence of SCN^-, indicating that the DNAzyme probe has a good selectivity for Pb^{2+} over other metal ions.

Applications. Pb^{2+} in the freshwater system is the most common lead pollution in the environment. To demonstrate the application potential of our DNAzyme probe in environmental analysis, we apply PS2.M to analyzing real freshwater samples (lake water). The results are shown in Figure 6. It is found that the Pb^{2+} content in the tested sample is too low to be probed by the DNAzyme. However, there is an obvious decrease in readout signal if different concentrations of Pb^{2+} are added into the sample. This suggests that our introduced DNAzyme-based method can be applied to the analysis of Pb^{2+} in environmental samples, with a sensitivity (the detection limit of Pb^{2+} is 100 nM) that is slightly lower than that in aqueous buffer.

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CONCLUSION

We have introduced a novel colorimetric and chemiluminescence (CL) Pb^{2+} sensor based on a Pb^{2+}-induced allosteric G-quadruplex DNAzyme (PS2.M). In the presence of K^+, PS2.M exhibits a superior DNAzyme activity, whereas Pb^{2+} induces K^+-stabilized PS2.M to undergo a conformational change that is accompanied by a sharp decrease in the DNAzyme activity. The cation-switched two states (active and inactive) of PS2.M allow us to utilize this G-quadruplex DNAzyme as a facile but effective sensor for Pb^{2+} detection with high sensitivity. With colorimetry, a detection limit of 32 nM (~7 ppb) for Pb^{2+} analysis is achieved, while a lower concentration (1 nM (i.e., 0.2 ppb)) of Pb^{2+} can be detected utilizing the CL method. In addition to high sensitivity, the DNAzyme-based sensor exhibits good selectivity for Pb^{2+} over other metal ions, with the assistance of the masking regent SCN^-.

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SUPPORTING INFORMATION AVAILABLE

Graphs showing the distinct effects of K^+ and Sr^{2+} cations on the catalytic activity of G-quadruplex DNAzyme in the ABTS−H_2O_2 reaction system (Figure S1) and the dependence of DNAzyme activty on the concentration of K^+ cations (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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